

SCIENCE FOR CERAMIC PRODUCTION

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PROCESSES OF PHASE FORMATION IN HEAT TREATMENT OF CHEMICALLY PRECIPITATED MIXTURES FOR ALUMINUM- AND CHROMIUM-MAGNESIUM SPINELS

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A comparative study of phase formation in aluminum- and chromium-magnesium spinels produced from chemically coprecipitated mixtures is performed. It is shown that the significant difference in the processes of formation of the specified spinels under thermal treatment is caused by the reaction between MgO and Al₂O₃ in precipitation, leading to the formation of crystal hydrate Mg₅Al₄O₁₁ · 15H₂O. The formation of chromium-magnesium spinel proceeds much more slowly and requires higher temperatures. It is established that fine chemical synthesis of spinels MgO · Al₂O₃ and MgO · Cr₂O₃ decreases the temperature of synthesis by 400 – 500 and 150 – 200°C, respectively, compared to traditional solid-phase synthesis.

One of the latest technological trends is using fine chemical synthesis based on chemical precipitation from solutions. This method is especially advisable in the synthesis of high-melting compounds, which include a number of spinel-type compounds that are of practical importance. Considering that the use of fine chemical synthesis based on chemical precipitation significantly modifies the mechanism of structure formation and the sequence of phase states under thermal treatment and knowing that these regularities for high-melting spinel compounds are insufficiently investigated, we have analyzed phase-formation processes in aluminum- and chromium-magnesium spinel for the purpose of developing scientific principles for using fine chemical synthesis in the production of ceramic materials based on spinel.

The choice of MgO · Al₂O₃ and MgO · Cr₂O₃ spinels for investigation was determined by the fact that Al₂O₃ and Cr₂O₃ are isostructural and can form a continuous series of solid solutions [1]. The phase diagram of the Al₂O₃ – Cr₂O₃ system and density variations in solid solutions of this system are shown in Fig. 1. It could be expected that the phase and structure formation regularities in mixtures obtained by chemical precipitation for these spinels will be similar; however, our study did not corroborate this hypothesis.

Most methods for synthesis of spinels are based on oxide components reacting under high temperatures. The wide application of such method is impeded by the difficulties of the

process related to very high temperatures of producing spinel and spinel-based ceramic materials.

The formation of spinel in solid-phase synthesis in the MgO – Al₂O₃ system starts at a temperature of 800 – 900°C and proceeds most intensely at 1300 – 1600°C. On further increase in temperature, the quantity of the spinel phase actually does not grow. The degree of transformation of MgAl₂O₄ at 1500°C is only 80%, at 1750°C — 86%, and at 1850°C — 88% [2]. The oxides interact by means of reciprocal diffusion of Mg²⁺ and Al³⁺ cation while oxygen ions remain immobile, the main diffusing component is Mg²⁺ and Al³⁺ cations while the oxygen ions stay immobile; the main diffusing component is Mg²⁺, whereas spinel is formed on Al₂O₃ grains. The synthesis kinetics is described by the Zhuravlev diffusion equation [3].

It is difficult to obtain dense ceramics based on spinel, although numerous attempts have been made using mineralizing agent, spray pyrolysis, or thermal treatment of polycrystalline samples [4, 5]. The sintering process, microstructure, phase composition, and properties of ceramics to a large extent depend on the production method [6], the ratio of the components, and the heat treatment conditions [3, 7 – 10]. Refractory and ceramic materials are usually produced from presynthesized aluminomagnesian spinel under firing within a temperature interval of 1650 – 1750°C [11].

The production of chromium-magnesian spinel from MgO and Cr₂O₃ also involves high temperatures of synthesis (1750 – 1800°C). A specific feature of the solid-phase syn-

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thesis of this spinel is the substantial increase in the amount of the reaction product (up to 7.4%), which increases the porosity and impedes the sintering of spinel-based materials [12, 13]. Even under such high-temperature synthesis, open porosity reaches 20–30%.

In using the coprecipitation method, components are precipitated from salt solutions in the form of poorly soluble hydroxides, carbonates, or oxalates. For each combination of precipitated elements it is necessary to select a particular precipitator, its concentration, the pH level of the solution, and the temperature conditions. The obtained precipitate is filtered and rinsed. Under a subsequent heat treatment, the synthesis is usually completely at a temperature that is 200–400°C lower than the temperature of producing the same compounds from powders in solid-phase synthesis and the resulting compounds have a high degree of homogeneity.

To synthesize aluminomagnesian spinel in the form of finely dispersed powder, the authors in [6] use the method of coprecipitation from concentrated solutions. The components were precipitated from aqueous solutions of magnesium sulfate and aluminum nitrate using an ammonia solution. The process of salt decomposition under the thermal treatment of the obtained powders ended at 1000–1100°C and the process of spinel formation ended at 1300°C. The sintering of ceramic samples based on spinel ended at 1600°C.

It is shown in [14] that, unlike the traditional method of synthesizing spinel powder MgAl_2O_4 by the solid-phase oxide reaction at 1600°C, the production of this powder by coprecipitation from aqueous solutions lowers the temperature of spinel synthesis to 1450°C.

According to the data in [7], in samples produced by mixing magnesium and aluminum hydroxide solutions, spinel MgAl_2O_4 is not identified even at a temperature of 800°C.

The authors in [2] have produced porous spinel by coprecipitation from magnesium and aluminum nitrate solutions. According to x-ray phase analysis, spinel is formed at 600–800°C, and yet it was impossible to obtain spinel of stoichiometric composition. However, according to [3], thermal decomposition of a mixture of magnesium and aluminum nitrates leads to the formation of spinel in the temperature interval of 300–500°C.

Generally, there are significant discrepancies in the literature regarding the starting temperature of spinel formation under the thermal treatment of coprecipitated mixtures and the temperature of completion of this process. Data on the production of chromium-magnesian spinel by chemical precipitation from solutions are not found in the literature. However, in this case as well we could expect a decrease in the temperature of synthesis of spinel MgCr_2O_4 from chemically coprecipitated mixtures.

In the course of the fine chemical synthesis of spinels in our studies we obtained precipitates from solutions $\text{MgCl}_2 - \text{AlCl}_3 - \text{H}_2\text{O}$ and $\text{MgCl}_2 - \text{Cr}(\text{NO}_3)_3 - \text{H}_2\text{O}$ with preset molar ratios of $\text{MgO} : \text{Al}_2\text{O}_3 = 1 : 1$ and $\text{MgO} : \text{Cr}_2\text{O}_3 = 1 : 1$ under the effect of the precipitator NH_4OH . The precipitates were rinsed from impurities and subjected to 1-h heat treat-

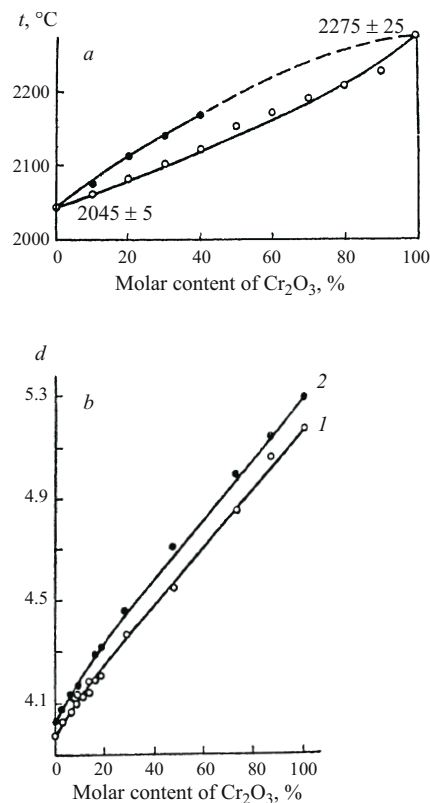


Fig. 1. Phase diagram of $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ system (a) and density d based on pycnometric (1) and x-ray diffraction data (2) of solid solutions in the system (b).

ment in the temperature interval of 300–1350°C for aluminomagnesium spinel and 300–1600°C for chromium-magnesium spinel.

It should be noted that the x-ray patterns of coprecipitated dried mixtures for the two spinels differ significantly. The diffraction patterns in the $\text{MgO} - \text{Al}_2\text{O}_3$ system contain peaks of the compound $\text{Mg}_5\text{Al}_4\text{O}_{11} \cdot 15\text{H}_2\text{O}$ (interplanar distances 0.474, 0.439, 0.256, 0.239, and 0.225 nm). Consequently MgO and Al_2O_3 start reacting while still in the solution and form a crystal hydrate.

The precipitate of the chromium-magnesian mixture is totally x-ray-amorphous; therefore, there is no reason to assume a probable reaction between MgO and Cr_2O_3 in the solution. These differences in the structure of the precipitates are clearly reflected in their filtering properties. The filtration rate grows in the presence of crystal hydrates.

Figure 2 shows the variation of the relative intensity of the main (100%) peaks in the patterns of heat-treated samples of spinels $\text{MgO} \cdot \text{Al}_2\text{O}_3$ (the peak with an interplanar distance of 0.2436 nm) and $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ (the peak with interplanar distance 0.2508 nm). The close values of the interplanar distances of 100% and 55% peaks (0.2021 and 0.2083 nm, respectively) may serve as evidence of the similarity of the main crystallochemical parameters for the experimental spinel structures. It should be noted that both spinels

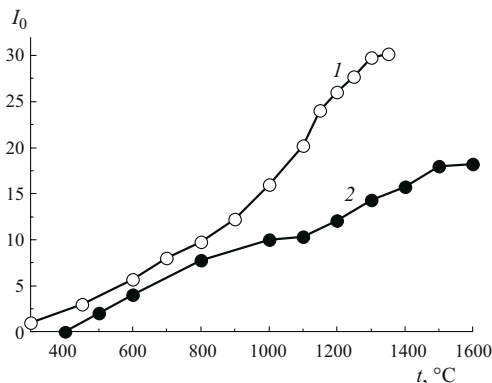


Fig. 2. Relative intensity of main 100% peaks on diffraction patterns versus the temperature of heat treatment of spinels $\text{MgO} \cdot \text{Al}_2\text{O}_3$ (1) and $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ (2).

belong to so-called normal spinels, in which the two-charge cations take tetrahedral positions and the three-charge cations take octahedral positions. However, the processes of formation of experimental spinels from coprecipitated precipitates under heat treatment are essentially different.

The first indications of the formation of spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ are observed under the thermal treatment of precipitates in the temperature interval of 400–450°C after the crystal hydrate $\text{Mg}_5\text{Al}_4\text{O}_{11} \cdot 15\text{H}_2\text{O}$ disintegrates at 320°C and the mixture becomes amorphous. On further increasing the heat treatment temperature to 800°C, the main peak gradually grows and then the spinel formation processes sharply intensify and reach their maximum at 1300°C. Actually under this temperature the formation of spinel as the only crystalline phase is completed. Upon increasing the heat treatment temperature to 1350°C, no changes were observed in the diffraction patterns.

Thus, the fine chemical synthesis of spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$ lowers the temperature of the completion of spinel formation by 400–500°C compared to traditional solid-phase synthesis.

The start of the formation of chromium-magnesium spinel MgCr_2O_4 is registered only at the temperature of 500°C and this process slowly grows up to 1000–1100°C. Then the process intensifies and ends only at the temperature of 1600°C, i.e., the formation of chromium-magnesium spinel is significantly slower and requires higher temperatures. However, the formation of chromium-magnesium spinel is also completed at a temperature that is 150–200°C lower than in solid-phase synthesis, although the difference is less than in the case of aluminum-magnesium spinel.

Thus, at the stage of coprecipitation, as well as in thermal treatment, the processes of formation of aluminomagnesium and chromium-magnesium spinel are essentially different and consist in the following:

- formation under coprecipitation of the intermediate compound $\text{Mg}_5\text{Al}_4\text{O}_{11} \cdot 15\text{H}_2\text{O}$ in the system $\text{MgO} - \text{Al}_2\text{O}_3$ and an x-ray amorphous precipitate in the system $\text{MgO} - \text{Cr}_2\text{O}_3$;

- activation of spinel formation processes under 800–900°C in the aluminomagnesium system and at 1000–1100°C in the chromium-magnesium system;

- completion of the processes of spinel formation at the temperatures of 1300 and 1600°C, respectively.

However, in both cases the use of fine synthesis accelerates the formation of spinel compared to solid-phase synthesis.

The slower formation of chromium-magnesium spinel from a chemically coprecipitated mixture under thermal treatment compared to aluminomagnesium spinel may be caused by the different degree of covalence of bonds emerging in the spinels. Indeed, judging by the electronegativity of the elements equal to 1.47 in aluminum, 1.56 in chromium, and 3.50 in oxygen [15], the Al–O bond is more polar than the Cr–O bond. Furthermore, the difference in the ionic radii is perceptible as well. This difference is larger between the magnesium ($r = 0.074$ nm) and aluminum ($r = 0.057$ nm) ions than between the magnesium and chromium ($r = 0.064$ nm) ions [16]. The latter reference data were used to calculate the ionic potential ϕ as the ratio of the charge of the ion to its radius, and the difference between these values was found for each system:

For the system $\text{MgO} - \text{Al}_2\text{O}_3$:

$$\Delta\phi = \phi(\text{Al}) - \phi(\text{Mg}) = 52.6 - 27.0 = 25.6.$$

For the system $\text{MgO} - \text{Cr}_2\text{O}_3$:

$$\Delta\phi = \phi(\text{Cr}) - \phi(\text{Mg}) = 46.9 - 27.0 = 19.9.$$

The greater the difference in the ionic potentials, the greater the difference in the acid-base properties of the ions [15]. Consequently, under coprecipitation, a salt-like compound resembling magnesium aluminate can be formed in the $\text{MgO} - \text{Al}_2\text{O}_3$ system, whereas coprecipitated hydroxides can be formed in the $\text{MgO} - \text{Cr}_2\text{O}_3$ system. Then the first compound will constitute mainly a crystalline precipitate and the second compound represents an amorphous precipitate.

Thus, the reactions between magnesium and aluminum ions under a hydroxide coprecipitation occurs already in the solution, whereas in the system $\text{MgO} - \text{Cr}_2\text{O}_3$ this does not occur. This is presumably the reason for the difference in behavior of the obtained compounds under subsequent heat treatment.

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